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*The Sol-Gel Process: Uniformity, Polymers and Applications, R.E. Morris Ed., Chap. 29,  
pp. 835-863, Nova Science Publishers, Inc. (2011)*

# AN INTRODUCTION TO THE STATISTICAL THEORY OF POLYMER NETWORK FORMATION

***Pierre Gilormini\****

Laboratoire Procédés et Ingénierie en Mécanique et Matériaux, CNRS,  
Arts et Métiers ParisTech, Paris (France)

## **Abstract**

A short but detailed introduction to the statistical theory of polymer network formation is given, including gel formation, gel structure, and sol fraction. Focus is put on the use of probability generating functions, and results that are of interest for polymer network elasticity are emphasized. Detailed derivations are supplied, and a simple 6-step procedure is provided, so that the reader is able to adapt and apply the theory to his own chemical systems, even if examples are given on polyurethanes essentially.

**Key Words:** gelation, network, polymers, polyurethane.

## **Introduction**

The statistical theory of polymer network formation may sometimes appear as too complicated, which limits its extensive use. The aim of this chapter is to give a short but detailed introduction to this theory, including gel formation, gel structure, and sol fraction, that is both straightforward and ready for use. An exhaustive account would be beyond an introductory chapter and extensive details can be found elsewhere, but it seemed useful to favor step-by-step applications of the theory to simple examples. The exposition uses slightly simplified notations, even if generality is lost temporarily, and differs on some points from

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\*E-mail address: pierre.gilormini@paris.ensam.fr

original papers, but results are unchanged. Indications are given on various extensions of the theory, but emphasis is put on basic ideas, with examples given on stepwise polymerization, and on polyurethanes especially. Moreover, stress is put on the results that are useful to the understanding of polymer network elasticity. The theory presented here uses probability generating functions, but some correspondences with the recursive approach of Macosko and Miller [1, 2] are given, which is summarized in a review by Queslel and Mark [3].

This Chapter has been inspired by the long review paper that K. Dušek published in 1989 [4], but his more recent papers have also been useful, especially one [5] where distributions of functionalities are considered. The paper that Ilavský and Dušek [6] published in 1983, where the entanglement factor is detailed, has also been very helpful. Some results of these articles are recovered below. The reader will also find complementary material in a book [7] published in 2002, and of course the seminal paper by Gordon [8] remains essential to the mathematics involved in the theory, but beyond the elements that are necessary below. These are only very few examples among numerous papers that have been published on the subject.

In what follows, the basic mathematical concepts that are necessary are presented first. Then, they are applied to the simplest case of a single type of monomer unit, before a simple polyurethane case is considered, without functionality distribution. This limitation is then removed before a summary of the method is given with a practical 6-step procedure. Finally, this procedure is applied to cases of various complexities in order to illustrate its possibilities. Even if telechelic polymers only are considered in this Chapter, without cyclization, to keep things simple, quite exhaustive derivations are given in this restrictive context, and it is hoped that they provide the reader with the elements that allow a further exploration of more elaborate theories of polymer network formation.

## Mathematical background

A very elementary part of the theory of stochastic branching processes is detailed here, with limitation to the only notions that are applied below extensively, and an exhaustive account can be found in the reference monograph by T.E. Harris [9], for instance. This theory is applied here to the growth of a random graph, and the simplest image that may be used in such an exposition is that of a family tree. Such trees are examples of stochastic graphs when one assumes that distribution of males and females at each generation obeys a random process. An essential phenomenon in this context is the possible ultimate extinction of a family.

Slightly special family trees are considered here, since the children of females only are of interest<sup>1</sup>. In this matriarchal society, a family tree begins with a primitive mother as an ancestor, and the offspring of females only are recorded at each subsequent generation. Therefore, ultimate extinction of a family is defined by all branches of the tree leading to males. Consider, for instance, that any primitive mother has 3 children and that any daughter

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<sup>1</sup>This contrasts with the very beginning of the theory, at the end of the 19th century, when F. Galton and H.W. Watson studied the extinction of family names. One reason for the present choice is that *mère*, in French, means both *mother* and *mer*, thus making a connection between genealogy and polymer science...



Figure 1. Various sets of children that a primitive mother (gray) may have, with either sons (white) or daughters (black). Birth order is not considered, that would triple each of the two central cases.

(or granddaughter, great-granddaughter, etc.) has 2 children. If  $p$  denotes the probability that a child is a female, then  $1 - p$  is the probability that the child is a male. The children of a primitive mother may be either 3 sons (and the family extincts immediately), or one daughter and two sons, or two daughters and one son, or three daughters. The probability of having 3 daughters is  $p^3$  and the one for three sons is  $(1 - p)^3$ . When daughters have brothers, several possibilities yield from birth order. If a daughter has two brothers, for instance, she may be the oldest child, the youngest, or intermediate, with a probability of  $(1 - p)^2 p$  in each case. Similarly, three possibilities come up when there is one son and two daughters, with probabilities of  $(1 - p)p^2$ . The whole set of possible combinations can be summarized as the coefficients of the following polynomial of a dummy variable  $z$ :

$$F_0(z) = (1 - p)^3 + 3(1 - p)^2 p z + 3(1 - p) p^2 z^2 + p^3 z^3. \quad (1)$$

In polynomial  $F_0(z)$ , the coefficient of  $z^k$  equals the probability for a primitive mother (hence subscript 0) to have  $k$  daughters, according to the above discussion. Not only does it gather the set of probabilities in a single expression (hence its name: *probability generating function*), with  $F_0(1) = 1$  consequently (the sum of all probabilities equals one), but this polynomial also has a very concise form:

$$F_0(z) = (1 - p + p z)^3 \quad (2)$$

as can be checked easily by developing the right-hand side. More generally, if the number of children of a primitive mother, and consequently her maximum number of daughters, is  $f$ , then the probability to have  $k$  daughters is the coefficient of  $z^k$  in  $(1 - p + p z)^f$ . In the  $f = 3$  case detailed above, the various possibilities can be represented graphically as in Figure 1.

The same procedure can be followed to count the possibilities that a daughter has when she becomes a mother (with two children): two boys (probability  $(1 - p)^2$ , with immediate extinction of the descendants), two girls (probability  $p^2$ ), or one boy and one girl (with two cases depending on the birth order, and therefore a total probability of  $2(1 - p)p$ ). Figure 2 shows these three possibilities, with probabilities that are gathered in the following polynomial:

$$F(z) = (1 - p)^2 + 2(1 - p)p z + p^2 z^2 = (1 - p + p z)^2 \quad (3)$$

where the coefficient of  $z^k$  is the probability for a non-primitive mother to have  $k$  daughters. The average number of daughters per mother can be deduced from the three plots shown in Figure 2 by summing the product of the number of daughters by the probability in each case:  $0 \times (1 - p)^2 + 1 \times 2(1 - p)p + 2 \times p^2$ , that is  $2p$ , which is also  $F'(1)$ , where  $F'$  denotes the derivative of  $F$ . In the more general case where a primitive mother may have  $f$  children,

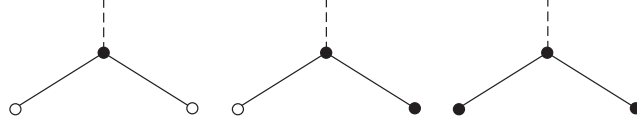


Figure 2. Various sets of children that a non-primitive mother may have: either two sons, or one son and one daughter, or two daughters.

the possibilities that are offered to the females in the following generations are given by the coefficients of  $(1 - p + pz)^{f-1}$  and the average number of daughters per mother is  $(f-1)p$ .

Even if a primitive mother has daughters, extinction of the family is nonetheless possible, since all branches of the family tree may lead to males. The probability  $e$  that the descendants of a non-primitive mother extinct can be obtained by considering the three situations shown in Figure 2: it is equal to the probability for a mother to have sons only, plus the probability that she has one son and one daughter whose descendants extinct (equal to  $e$  times the probability  $p$  to have a daughter), plus the probability that she has two daughters whose descendants extinct (equal to  $e^2$  times the probability  $p^2$  to have two daughters). Therefore, the probability of extinction obeys the following equation

$$e = (1 - p)^2 + 2(1 - p)pe + p^2e^2 \quad \text{or, equivalently,} \quad e = F(e) \quad (4)$$

with two roots:  $e = 1$ , that does not depend on  $p$  and is consequently excluded since it predicts extinction even when each generation has daughters only, and

$$e = \left( \frac{1}{p} - 1 \right)^2. \quad (5)$$

It can be observed first that extinction is less probable when daughters get more probable, as expected. If it is impossible to have sons (daughters only,  $p = 1$ ) extinction is impossible ( $e = 0$ ) but if sons and daughters are equally probable ( $p = 1/2$ ) extinction is unavoidable ( $e = 1$ ) because the average number of daughters per mother ( $2p$ ) is 1, reaching the limit of a stable population growth. If  $p$  is lower than  $1/2$ , extinction is even more a certitude, and the values of  $e$  given by (5) that are larger than 1 must be interpreted as being equal to 1 (extinction is sure:  $e = 1$ ). It is now possible to compute the probability  $s$  that the whole family of a primitive mother extincts, by weighting the probability of occurrence of each plot in Figure 1 by  $e$  raised to a power equal to the corresponding number of daughters, since the latter are as many non-primitive mothers whose descendants may extinct:

$$s = (1 - p)^3 + 3(1 - p)^2pe + 3(1 - p)p^2e^2 + p^3e^3 \quad \text{or, equivalently,} \quad s = F_0(e) \quad (6)$$

with  $s = 0$  if  $p = 1$  and  $s = 1$  if  $p \leq 1/2$ , using the corresponding  $e$  values, which extends the above conclusions to the whole tree.

In the more general case with  $f$  children per primitive mother, the probability that the descendants of a non-primitive mother extinct is obtained the same way as above and is the root (non equal to 1) of

$$(1 - p + pe)^{f-1} = e \quad \text{or, equivalently,} \quad e^{\frac{1}{f-1}} - pe + p - 1 = 0 \quad (7)$$

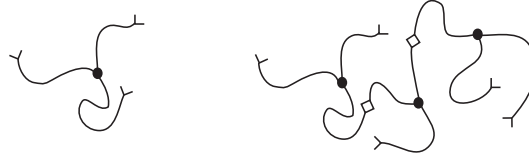


Figure 3. Monomer (left) and trimer (right) in the case of a single, trifunctional, kind of reactive molecule. Terminal reactive groups are shown as corners, links are shown as white squares.

which can be recast into

$$p = \frac{e^{\frac{1}{f-1}} - 1}{e - 1} \quad \text{that gives} \quad p = \frac{1}{\sum_{k=1}^{f-1} e^{\frac{k-1}{f-1}}} \quad (8)$$

after simplification by  $e - 1$ , by taking  $u = e^{\frac{1}{f-1}}$  and  $i = f - 1$  in  $u^i - 1 = (u - 1) \sum_{k=1}^i u^{k-1}$ , which is easy to obtain. The final one-to-one relation between  $e$  and  $p$  shows that the solution is unique, here again  $e$  decreases when  $p$  increases (since  $p$  decreases when  $e$  increases), and one has  $e = 0$  when  $p = 1$  and  $e = 1$  when

$$p = \frac{1}{f - 1} \quad (9)$$

since the denominator is then the sum of  $f - 1$  terms that are all equal 1. Now that the probability of extinction  $e$  for a non-primitive mother is obtained, the probability  $s$  that the number of descendants of a primitive mother is finite is obtained as above, by considering the various possibilities at the first generation and weighting by  $e$  raised to the corresponding number of daughters, which gives

$$s = (1 - p + pe)^f = F_0(e) = e^{\frac{f}{f-1}} \quad (10)$$

where the last expression has been obtained by noting that  $F_0(z) = F(z)^{\frac{f}{f-1}}$ . Therefore, the extreme probability values for the whole tree (descendants of a primitive mother),  $s = 0$  and  $s = 1$ , are obtained in the same conditions as for any subtree (descendants of a non-primitive mother),  $e = 0$  and  $e = 1$ , as already noted in the  $f = 3$  case above. Consequently,  $s = 0$  (the family is immortal certainly) if  $p = 1$ , and  $s = 1$  (the family tree is inevitably finite) if  $p \leq 1/(f - 1)$ .

The above results are sufficient to pass now from preliminary genealogical considerations to polymer applications.

## A first application

Consider the condensation of a very large number of monomer units with 3 equally reactive functional groups. Between the initial stage where no functional group has reacted yet and the final stage where reaction is complete, a mixture of molecules with various numbers of connected monomer units develops. Figure 3 shows a star-shaped monomer, with three

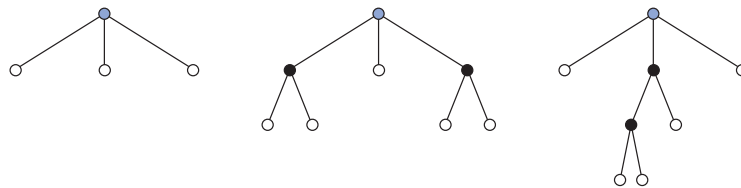


Figure 4. Graphs representing the two molecules of Figure 3: primitive mother with sons only (monomer), and two possibilities for three-mother families (trimer), with different choices for the primitive mother and either two or three subsequent generations.

arms of equal length, for instance, and a trimer. If cyclization is excluded, the various molecules formed can be represented as graphs similar to the family trees discussed in the previous Section, as illustrated in Figure 4. In such trees, the number of mothers is equal to the number of monomer units involved, and the numbers of daughters and sons are equal to the numbers of reacted and unreacted functional groups, respectively. A polymer molecule can be represented by several graphs, depending on the monomer unit that is taken as the primitive mother, and this affects the number of generations, as illustrated also in Figure 4.

Since all functional groups are assumed to have the same reactivity and the number of monomer units considered is very large, the probability  $p$  to have daughters corresponds here to the probability that a group has reacted, and is therefore equal to the fraction  $x$  of groups that have undergone reaction at the stage considered. Consequently,  $x$ , the extent of reaction, is henceforth used instead of  $p$ . It should be noted that the purpose here is a statistical description of the distribution of polymeric molecules in the system, taking advantage of an initial number of monomers so large that it can be considered as infinite; the purpose is not to follow the evolution of given molecules when  $x$  increases from 0 to 1. The extinction of a family that has been discussed in the previous Section corresponds now to a molecule being comprised of a finite number of monomer units, i.e., belonging to the sol phase. In opposition, a mother with an infinite number of descendants corresponds to a monomer unit in the gel phase. The condition for gelation to occur can thus be deduced directly from the analysis in the above Section, where it has been found that an infinite family is possible for  $p > 1/2$ : gelation occurs when the fraction of reacted groups reaches the value  $x_g = 1/2$ . More generally, relation (9) leads to the Flory condition [10] for  $f$ -functional monomer units:

$$x_g = \frac{1}{f-1}. \quad (11)$$

Once the gel has formed, the fraction of sol (soluble) phase, which is the fraction of monomer units that belong to molecules of finite size, can be obtained easily: it is merely equal to  $s$  defined by (10), which can be rewritten in the present context as

$$s = (1-x)^3 + 3(1-x)^2 x e + 3(1-x) x^2 e^2 + x^3 e^3 = \left( \frac{1}{x} - 1 \right)^3 \quad (12)$$

with the last expression, also given by Flory [11], obtained by using (5) where  $x$  replaces  $p$ . Actually, the expanded expression of  $s$  in (12) adds up the respective probabilities for a monomer unit to have from 0 to 3 reacted groups with, in each case, these groups giving rise

to finite subtrees, which is precisely the probability for a monomer unit selected at random from the system to belong to the sol phase. Thus, not only does (12) give the sol fraction, which decreases from 1 (up to the gel point,  $0 \leq x \leq x_g$ ,  $e$  must be taken equal to 1) to 0 (full conversion,  $x = 1$ ), but its various terms also give some information about the structure of the sol phase. The simplest is the first term, equal to  $F_0(0)$ , which is merely the fraction of unreacted monomers. The second term counts the number of terminations of the finite trees, where a single group has reacted and two remain unreacted, the third term gives the length of the branches, since twice reacted monomer units form chains, and the last term counts nodes, with three reacted groups from which three chains stem. Of course, this information is statistical only, and relates to averages. These actually are number averages here, because the latter yield directly from the statistical approach and are given by simple formulae, whereas molar or mass fractions are considered in the following Sections. They can be deduced from number averages, and the three quantities coincide in the present simple case of a single type of monomer unit.

By definition, a monomer unit that belongs to the gel phase has at least one reacted group with infinite continuation, i.e., a series of linked monomer units connects it to the boundaries of the reaction vessel, in practice. If it has only one such reacted group, it belongs to a dangling chain, since the other possible reacted groups have finite continuations. If the monomer unit has two reacted groups with infinite continuations, it belongs to an elastically active chain. It gives rise to a dangling chain if the third group has reacted (with finite continuation). Finally, three reacted groups giving rise to as many infinite chains define a node of the elastically active network. The fractions of these various types of monomer units in the gel phase can be evaluated easily by considering Figure 1, where the leftmost scheme is excluded since belonging to the gel phase requires at least one reacted group, of course. Using the probabilities  $e$  and  $1 - e$  for finite and infinite continuations, respectively,

$$d = 3(1 - x)^2 x(1 - e) + 2 \times 3(1 - x) x^2(1 - e)e + 3 \times x^3(1 - e)e^2 = (1 - e)F'_0(e) \quad (13)$$

gives the fraction of monomer units that belong to dangling chains. Coefficients 2 and 3 in front of the second and third terms come from the possible choices for the reacted group (among 2 or 3) with infinite continuation. The first term corresponds to monomer units that terminate dangling chains, the second one to intermediates along branches, and the last term to (elastically inactive) nodes belonging to dangling chains. The replacement of  $e$  with (5) gives

$$d = 3 \left( \frac{1}{x} - 1 \right)^2 \left( 2 - \frac{1}{x} \right) \quad (14)$$

for  $x > 1/2$  only, since  $d = 0$  when there is no gel. This fraction reaches a maximum for  $x = 3/5$  before decreasing back to 0 when  $x = 1$  (all chains are elastically active when reaction is complete). Similarly, the fraction  $a$  of monomer units that belong to elastically active chains but are not nodes of the active network is deduced from the two rightmost schemes in Figure 1, since at least two reacted groups are required, and is given by

$$a = 3(1 - x) x^2(1 - e)^2 + 3 \times x^3(1 - e)^2 e = 3 \left( \frac{1}{x} - 1 \right) \left( 2 - \frac{1}{x} \right)^2 \quad (15)$$

for there are 3 possible choices for the reacted group with finite continuation in the third scheme in Figure 1. The two terms in (15) again have immediate interpretations: the first



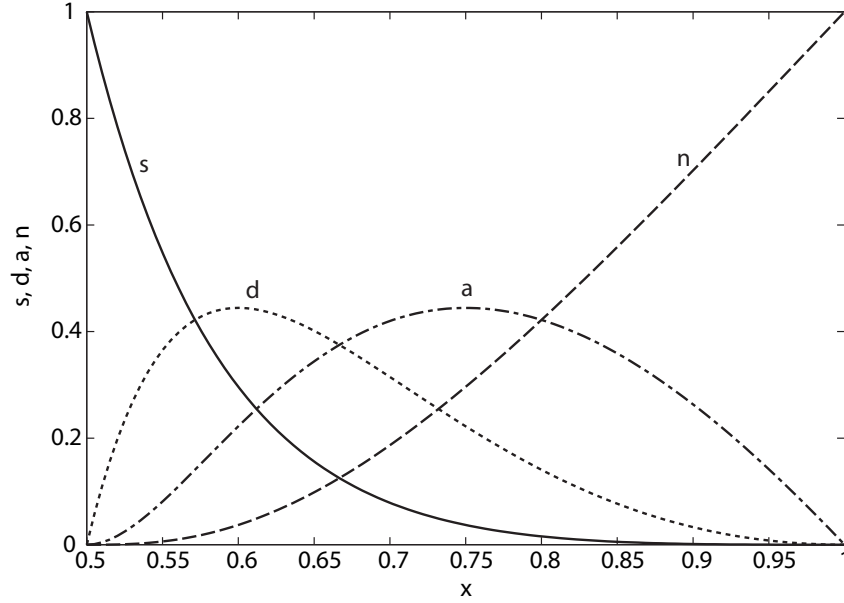


Figure 5. Variations of the various fractions of trifunctional monomer units when polymerization proceeds beyond the gel point: those belonging to the sol ( $s$ ), the dangling chains ( $d$ ), the elastically active chains ( $a$ ), the active nodes ( $n$ ).

one corresponds to monomer units that are intermediates between triple nodes and from which an unreacted arm stems, whereas the second term is for monomer units from which dangling chains originate. Finally, the fraction of monomer units that form elastically active nodes is obtained by considering the rightmost scheme in Figure 1 only, since 3 reacted nodes are necessary, each with infinite continuation:

$$n = x^3(1 - e)^3 \quad \text{hence} \quad n = \left(2 - \frac{1}{x}\right)^3. \quad (16)$$

Additional terms would appear for functionalities larger than 3, because more than 3 infinite chains may stem from an active node; this will be considered a later Section. All these fractions, which are defined for  $x > x_g$ , which fulfill the balance equation for the total number of monomer units  $s + d + a + n = 1$ , and which are illustrated in Figure 5, can be gathered in the following polynomial

$$\tilde{F}_0(z) = s + dz + az^2 + nz^3 = [1 - x + xe + x(1 - e)z]^3 = F_0(e + (1 - e)z) \quad (17)$$

where the coefficient of  $z^k$  (with a  $(1 - e)^k$  term) gives the probability for a monomer unit to have  $k$  links with infinite continuations.

Let now these results be applied to the theory of rubber elasticity. First, the number  $\nu_e$  of moles of elastically active chains is expressed from the molar mass  $M$  of the monomer and the mass density  $\rho$  of the mixture, for a given extent of reaction  $x$ . The number of elastically active chains is equal to  $3n/2$  times the total number of monomer units in the system, since each active chain has its two ends connected to a trifunctional active node,

which gives, using (16),

$$\nu_e = \frac{3}{2} \frac{\rho}{M} \left(2 - \frac{1}{x}\right)^3 \quad (18)$$

with  $(3\rho)/(2M)$  moles of elastically active chains per unit volume when reaction is complete and each chain is made of two arms of a monomer unit connected by one link, that is the shortest possible chain length. The expression given by Dossin and Graessley [12], and used by [3] and [6] for instance, for the elastic shear modulus of the network is

$$G = \left(\frac{f_n}{2} - h\right) n \frac{RT}{V} + \varepsilon T_e RT \quad (19)$$

with our notations, where  $V$  is the gel volume,  $T$  denotes absolute temperature,  $R$  the gas constant,  $f_n$  the average functionality of active nodes, (with  $f_n = f = 3$  in the present case). Parameter  $h$ , introduced in [12], varies from 0 to 1 and allows a continuous variation from the affine theory of rubber elasticity to the phantom network theory of Flory [13]. Parameter  $\varepsilon$ , introduced by Langley [14], accounts for an entanglement effect between elastically active chains in the case of a perfect network, if they are long enough. Factor  $T_e$ , between 0 and 1, weights this effect when the network is imperfect; it is proportional to the probability that two elastically active chains cross, and is therefore equal to the square of the ratio between the lengths of the elastically active chains in the imperfect and perfect networks, respectively.

In the simple case considered in this Section, the entanglement factor is obtained easily by taking a monomer arm as unit length (the unit can be chosen arbitrarily, since a length ratio is computed), assuming that all arms (3 per monomer unit) have the same lengths. Each monomer unit belonging to an elastically active chain without being an active node contributes with 2 unit lengths, and each node contributes with 3, which gives  $2a + 3n$  moles of unit lengths per initial mole of monomers. In a perfect network, all nodes are active, leading to 3 moles of unit lengths per initial mole of monomers. The ratio of these two quantities raised to power 2 gives the  $T_e$  coefficient:

$$T_e = \left(\frac{2}{3}a + n\right)^2 = \frac{1}{x^2} \left(2 - \frac{1}{x}\right)^4 \quad (20)$$

which evolves from 0 at the gel point ( $x = 1/2$ ) to 1 at full conversion ( $x = 1$ ). Figure 6 compares the variations of  $T_e$  and  $n$  during gel growth: the two quantities are close and consequently the values of the  $h$  and  $\varepsilon$  parameters will have a moderate influence on the shape of the variations of the shear modulus  $G$  in the present simple case, and will affect its amplitude essentially.

The above entanglement factor can readily be extended to the more general case of  $f$ -functional star-shaped monomer units where the  $f \geq 2$  arms have the same length. The molar fraction of monomer units with  $k$  branches having infinite continuations is the coefficient of  $z^k$  in

$$\tilde{F}_0(z) = [(1 - x + ex) + x(1 - e)z]^f = \sum_{k=0}^f C_f^k (1 - x + ex)^{f-k} x^k (1 - e)^k z^k \quad (21)$$

where  $C_f^k$  denotes a binomial coefficient, and they belong to elastically active chains if  $k \geq 2$ , otherwise they are connected to the network on one side only and consequently

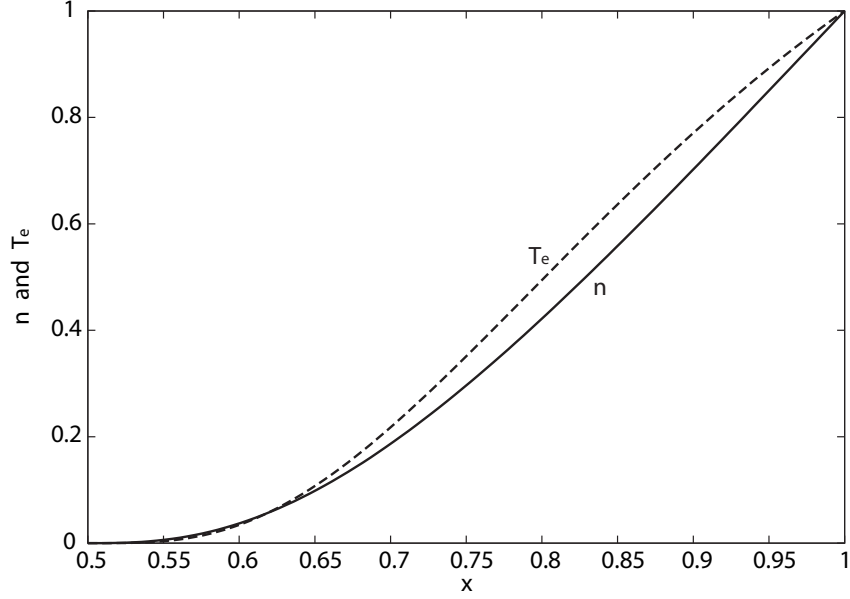


Figure 6. Variations of the fraction  $n$  of monomer units that are elastically active nodes of the network and of the entanglement factor  $T_e$  during gel growth, in the simple case of one kind of trifunctional monomer unit.

belong to dangling chains. Each of these monomer units contributes with  $k$  arms to the elastically active chains and, using an arm as unit length, the total length of the elastically active chains is

$$\lambda(r, x) = \sum_{k=2}^f C_f^k k (1 - x + xe)^{f-k} x^k (1 - e)^k. \quad (22)$$

Taking the derivative of (21) with respect to  $z$  leads to two equivalent expressions

$$\begin{aligned} \tilde{F}'_0(z) &= f[(1 - x + ex) + x(1 - e)z]^{f-1} x(1 - e) = \\ &= \sum_{k=1}^f k C_f^k (1 - x + xe)^{f-k} x^k (1 - e)^k z^{k-1} \end{aligned} \quad (23)$$

which, when setting  $z = 1$ , give

$$fx(1 - e) = \sum_{k=1}^f k C_f^k (1 - x + xe)^{f-k} x^k (1 - e)^k = f(1 - x + ex)^{f-1} x(1 - e) + \lambda \quad (24)$$

hence

$$\lambda(r, x) = fx(1 - e)[1 - (1 - x + ex)^{f-1}] = fx(1 - e)[1 - F(e)] = fx(1 - e)^2 \quad (25)$$

by using (7a). Consequently,  $\lambda(1, 1) = f$  and finally

$$T_e = x^2(1 - e)^4. \quad (26)$$

It may be noted that functionality does affect  $T_e$  through  $e$ , and the previous result (20) is recovered when  $f = 3$ .

## A simple polyurethane case

Consider a polyurethane produced by reaction between bifunctional diols (one OH group at each end of the molecule) and triisocyanates (three NCO groups that are likely to create links by reacting with diol OH groups). Let  $n_D$  and  $n_I$  denote the molar fractions of diols and triisocyanates in the mixture, with  $n_D + n_I = 1$ . The ratio  $r = [\text{NCO}]/[\text{OH}] = (3n_I)/(2n_D)$  identifies the proportions of functional groups in the mixture and  $r \leq 1$  will be assumed here, which means that there will never be an excess of NCO groups<sup>2</sup>. Let  $x$  denote the fraction of reacted NCO groups; the fraction of reacted OH groups is, therefore, equal to  $rx$ , with a fraction of  $1 - r$  OH groups left unreacted when all NCO groups have reacted ( $x = 1$ ), since each reaction consumes one group of each type. If, here again, equal reactivities are assumed, which excludes that the last NCO group is less reactive after two groups of an isocyanate molecule have reacted, for instance, the results given heretofore can be adapted readily.

The polynomials that gather the probabilities that a triisocyanate unit selected at random from the mixture has 0, 1, 2, or 3 reacted groups and for a randomly picked diol to have 0, 1, or 2 reacted groups are

$$F_{0I}(z) = (1 - x + xz)^3 \quad \text{and} \quad F_{0D}(z) = (1 - rx + rxz)^2 \quad (27)$$

by adapting (2) to probabilities  $p = x$  and  $p = rx$ , respectively. The polynomials that describe the probabilities to have more than one reacted group in a triisocyanate or diol unit are

$$F_I(z) = (1 - x + xz)^2 \quad \text{and} \quad F_D(z) = 1 - rx + rxz \quad (28)$$

respectively, by adapting (3). The condition for extinction is obtained by writing that the possible additional links of a triisocyanate that has already reacted once and the possible second link of an already reacted diol have finite continuations:

$$e_I = (1 - x)^2 + 2(1 - x)xe_D + x^2e_D^2 \quad \text{and} \quad e_D = 1 - rx + rxe_I \quad (29)$$

where the occurrence of  $e_D$  in the first expression and of  $e_I$  in the second owes to the fact that the descendants of a triisocyanate reacted group are the descendants of the linked diol, and vice versa. This renders the alternation between isocyanate and diol units in polyurethane. These two equations can also be written more concisely as

$$e_I = F_I(e_D) \quad \text{and} \quad e_D = F_D(e_I) \quad (30)$$

and their solutions between 0 and 1 (excluding the trivial  $e_I = e_D = 1$  solution) are

$$e_I = \left(1 - \frac{1}{rx^2}\right)^2 \quad \text{and} \quad e_D = 1 - \frac{2}{x} + \frac{1}{rx^3}. \quad (31)$$

The gel condition  $e_I(x) = e_D(x) = 1$  is therefore obtained when reaction has proceeded up to

$$x_g = \frac{1}{\sqrt{2r}}. \quad (32)$$

---

<sup>2</sup>In the study of a mixture with an excess of NCO groups,  $r$  can be defined as  $[\text{OH}]/[\text{NCO}]$  in order to keep  $x$ , still defined as the fraction of reacted majority groups, and  $rx$  in the same ranges.

As a consequence, a gel is obtained for complete reaction ( $x = 1$ ) if the mixture is such that  $1/2 < r \leq 1$ .

More generally, if  $f$ -functional molecules are reacted with  $g$ -functional molecules, with  $f \geq 2$  and  $g \geq 2$ , the mixture is described by the  $r = (f n_f)/(g n_g)$  ratio and the extinction probabilities are given by

$$e_f = (1 - x + x e_g)^{f-1} \quad \text{and} \quad e_g = (1 - rx + rx e_f)^{g-1} \quad (33)$$

which can also be rewritten, by developing the terms in parentheses,

$$e_f = 1 + \sum_{k=1}^{f-1} C_{f-1}^k (e_g - 1)^k x^k \quad \text{and} \quad e_g = 1 + \sum_{l=1}^{g-1} C_{g-1}^l (e_f - 1)^l (rx)^l \quad (34)$$

which are also equivalent to

$$\frac{e_f - 1}{e_g - 1} = \sum_{k=1}^{f-1} C_{f-1}^k (e_g - 1)^{k-1} x^k \quad \text{and} \quad \frac{e_g - 1}{e_f - 1} = \sum_{l=1}^{g-1} C_{g-1}^l (e_f - 1)^{l-1} (rx)^l \quad (35)$$

leading to

$$\left[ (f-1)x + \sum_{k=2}^{f-1} C_{f-1}^k (e_g - 1)^{k-1} x^k \right] \times \left[ (g-1)rx + \sum_{l=2}^{g-1} C_{g-1}^l (e_f - 1)^{l-1} (rx)^l \right] = 1. \quad (36)$$

The gel condition  $e_f = e_g = 1$  is thus obtained when  $x$  takes the value

$$x_g = \frac{1}{\sqrt{r(f-1)(g-1)}}, \quad (37)$$

which is a classical result (see [4] or [7], for instance), and (32) is recovered if  $f = 3$  and  $g = 2$ . Therefore, a gel is obtained when reaction is complete if

$$r > \frac{1}{(f-1)(g-1)}. \quad (38)$$

If a triisocyanate molecule has no link with infinite continuation, it belongs to the sol phase and this occurs with a probability of  $F_{0I}(e_D)$ , by adapting (10) to the triisocyanate-diol alternation, and similarly for a diol molecule with a probability of  $F_{0D}(e_I)$ . These two number fractions can be used to compute the mass fraction  $m_s$  of sol phase, by weighting with the mass fractions of isocyanate and diol in the system

$$m_I = \frac{M_I n_I}{M_I n_I + M_D n_D} \quad \text{and} \quad m_D = \frac{M_D n_D}{M_I n_I + M_D n_D} \quad (39)$$

where  $M_I$  and  $M_D$  denote the molar masses of the two components, hence

$$m_s = F_{0I}(e_D) m_I + F_{0D}(e_I) m_D \quad (40)$$

and, therefore,

$$m_s = \left(-1 + \frac{1}{rx^2}\right)^3 m_I + \left(1 - \frac{2}{x} + \frac{1}{rx^3}\right)^2 m_D \quad (41)$$

which does give  $m_s = 1$  at the gel point ( $x = 1/\sqrt{2r}$ ). At the end of reaction ( $x = 1$ ),  $m_s$  is not equal to the initial excess mass fraction of diol  $(1 - r)m_D$  if  $r < 1$ : for non stoichiometric conditions, the gel at the end of reaction coexists with a sol phase that contains molecules where isocyanates and diols are linked.

Once the gel is formed, the various number fractions of interest are given by the coefficients of

$$\begin{aligned} \tilde{F}_{0I}(z) &= [1 - x + xe_D + x(1 - e_D)z]^3 \\ \text{and } \tilde{F}_{0D}(z) &= [1 - rx + rxe_I + rx(1 - e_I)z]^2 \end{aligned} \quad (42)$$

by adapting (17) to triisocyanate and diols, respectively, still keeping in mind that an isocyanate extends toward a diol, and vice versa. Of course, the above sol fractions are obtained as the constant terms in (42),  $\tilde{F}_{0I}(0) = F_{0I}(e_D)$  and  $\tilde{F}_{0D}(0) = F_{0D}(e_I)$ , and the number of moles of triple nodes in the gel phase, which are tri-reacted isocyanates, is readily obtained from the coefficient of  $z^3$  in  $\tilde{F}_{0I}(z)$ :

$$n = x^3(1 - e_D)^3 n_I = \left(2 - \frac{1}{rx^2}\right)^3 n_I. \quad (43)$$

The  $3n/2$  moles of elastically active chains in the mixture, which has a mass density  $\rho$ , lead to the following number of moles of elastically active chains per unit volume:

$$\nu_e = \frac{3}{2} \frac{\rho n}{M_I n_I + M_D n_D} = \frac{3\rho r}{2rM_I + 3M_D} \left(2 - \frac{1}{rx^2}\right)^3. \quad (44)$$

The molar fraction of the elastically active network, including both chains and nodes, is deduced readily from the coefficients of  $z^2$  and  $z^3$  in (42), respectively:

$$m_a = [3(1 - x + xe_D)x^2(1 - e_D)^2 + x^3(1 - e_D)^3]m_I + r^2x^2(1 - e_I)^2m_D \quad (45)$$

or, equivalently

$$m_a = \left(2 - \frac{1}{rx^2}\right)^2 \left[ \left(-1 + \frac{2}{rx^2}\right) m_I + \frac{1}{x^2} m_D \right]. \quad (46)$$

Finally, the mass fraction of dangling chains, excluding the isocyanate units they stem from, which belong to active chains, is given by the  $z$  terms in (42):

$$m_d = 3(1 - x + xe_D)^2 x(1 - e_D)m_I + 2(1 - rx + rxe_I)rx(1 - e_I)m_D \quad (47)$$

which, from (31), gives

$$m_d = \left(2 - \frac{1}{rx^2}\right) \left[ 3 \left(-1 + \frac{1}{rx^2}\right)^2 m_I + \frac{2}{x} \left(1 - \frac{2}{x} + \frac{1}{rx^3}\right) m_D \right] \quad (48)$$

and it can be checked that  $m_s + m_a + m_d = 1$  does apply.

The entanglement factor can also be obtained, since the total length of elastically active chains per mole of mixture adds up the contributions of the three arms of each elastically active triple node, the two arms of intermediate triisocyanates along elastically active chains, and the diols in the latter chains. Therefore, the same constitutive elements as in (45) are obtained and give

$$\lambda(r, x) = 3\tau x^3(1 - e_D)^3 n_I + 6\tau(1 - x + x e_D)x^2(1 - e_D)^2 n_I + r^2 x^2(1 - e_I)^2 n_D \quad (49)$$

by taking a diol as unit length, assuming that all diols have the same length, and denoting  $\tau$  the length of a triisocyanate arm (assumed all equal) with this unit. Replacing  $e_I$  and  $e_D$  in the above expressions, and using  $n_I = 2r/(2r + 3)$  et  $n_D = 3/(2r + 3)$ , which are readily obtained, (49) is recast as

$$\lambda(r, x) = \frac{3}{x^2} \left( 2 - \frac{1}{rx^2} \right)^2 \frac{2\tau + 1}{2r + 3} \quad (50)$$

hence the entanglement factor:

$$T_e = \left[ \frac{\lambda(r, x)}{\lambda(1, 1)} \right]^2 = \frac{1}{x^4} \left( 2 - \frac{1}{rx^2} \right)^4 \left( \frac{5}{2r + 3} \right)^2 \quad (51)$$

which does not depend on the relative length  $\tau$  of triisocyanate arms compared to diols. This is not surprising: be it in the imperfect or perfect network, an elastically active chain is a repeated sequence of one isocyanate arm followed by one diol followed by one isocyanate arm, and this defines another unit length (equal to  $2\tau + 1$  times the previous one) that vanishes when the ratio of the total lengths in the imperfect and perfect networks is performed. Consequently, the lengths of isocyanate arms and diols are not relevant in the  $T_e$  factor. In the examples considered below,  $\tau$  is used nevertheless as a temporary and convenient variable in the intermediate  $\lambda$  computation. In stoichiometric conditions ( $r = 1$ ),  $T_e$  and  $n$  have similar magnitudes during gel growth, which is similar to the result obtained in the simple homopolymer case of the previous Section, since (51) and (43) are equivalent to (20) and (16) where  $x$  is replaced by  $x^2$ , which modifies the shapes of the curves in Figure 6 marginally, with now  $x$  between  $\sqrt{2}$  and 1. Moreover, off stoichiometry but at full conversion ( $x = 1$ ), Figure 7 shows similar trends for  $n$  and  $T_e$ . Consequently, the same conclusions as in the previous Section are obtained as far as the influences of parameters  $h$  and  $\varepsilon$  are concerned.

The entanglement factor can also be calculated in the general case of star-shaped  $f$ -functional units reacting with  $g$ -functional units, with  $f$  and  $g$  larger than 2. For the total length of elastically active chains, one gets

$$\begin{aligned} \lambda_f(r, x) &= f x(1 - e_g)[1 - F_f(e_g)] n_f = f x(1 - e_g)(1 - e_f) n_f \\ \text{and } \lambda_g(r, x) &= \tau g r x(1 - e_f)[1 - F_g(e_f)] n_g = \tau g r x(1 - e_f)(1 - e_g) n_g \end{aligned} \quad (52)$$

as the contributions of  $f$ -functional and  $g$ -functional units, respectively (note that  $rx$  replaces  $x$  for the latter), using an arm of  $f$ -functional molecule as unit length, with  $\tau$  denoting the length of an arm of  $g$ -functional molecule. Therefore,

$$\lambda(r, x) = \lambda_f(r, x) + \lambda_g(r, x) = f g r x(1 - e_g)(1 - e_f) \frac{\tau + 1}{gr + f} \quad (53)$$

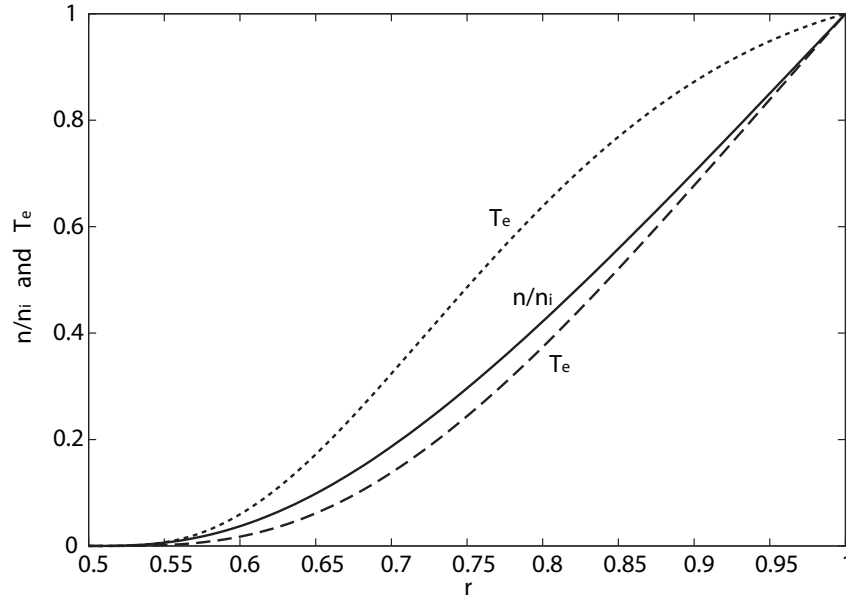


Figure 7. Fraction  $n/n_I$  of triisocyanates that are nodes of the active network (unbroken line) and entanglement factor  $T_e$  (broken line), for full conversion with an excess of OH, when composition of the triisocyanate-diol mixture evolves. The entanglement factor  $T_e$  is also shown (dotted line) for the diisocyanate-triol mixture that is considered later.

using  $n_f = gr/(gr + f)$  and  $n_g = f/(gr + f)$ , which yield from  $n_f + n_g = 1$  and  $r = (fn_f)/(gn_g)$ . Consequently,  $\lambda(1, 1) = fg(\tau + 1)/(g + f)$  and

$$T_e = r^2 x^2 (1 - e_g)^2 (1 - e_f)^2 \left( \frac{g + f}{gr + f} \right)^2 \quad \text{with } f \geq 3, g \geq 3, r = \frac{fn_f}{gn_g} \leq 1 \quad (54)$$

which does not depend on  $\tau$ , as expected. This expression simplifies slightly when one type of units is bifunctional. Assume for instance that  $g = 2$ ; the contribution of bifunctional molecules is directly given by the coefficient of  $z^2$  in  $\tilde{F}_{0g}(z)$ , that is

$$\lambda_g = \tau r^2 x^2 (1 - e_f)^2 n_g = \tau (1 - e_g)^2 n_g \quad (55)$$

using  $e_g = 1 - rx + rxe_f$ , as given by (29). Therefore,

$$\lambda(r, x) = \lambda_f(r, x) + \lambda_g(r, x) = 2f(1 - e_g)^2 \frac{\tau f + 2}{2r + f} \quad (56)$$

using  $n_f = 2r/(2r + f)$  and  $n_g = f/(2r + f)$ . Consequently,  $\lambda(1, 1) = 2f(\tau f + 2)/(2 + f)$  and

$$T_e = (1 - e_g)^4 \left( \frac{2 + f}{2r + f} \right)^2 \quad \text{with } f \geq 3 \quad \text{and } r = \frac{fn_f}{2n_g} \leq 1 \quad (57)$$

which recovers (51) for  $f = 3$ . Finally, (57) can also be obtained directly from (54) by changing  $g$  into 2 and using  $(1 - e_g) = rx(1 - e_f)$  that yields from (34). It should be noted, however, that these operations do not change (53) into (56) because a bifunctional



molecule is not star-shaped, actually. Consider now that  $f = 2$ , the bifunctional molecules are minority, which leads now to

$$T_e = r^2(1 - e_f)^4 \left( \frac{g+2}{gr+2} \right)^2 \quad \text{with } g \geq 3 \quad \text{and} \quad r = \frac{2n_f}{gn_g} \leq 1 \quad (58)$$

which can also be deduced from (54) by changing  $f$  into 2 and using  $(1 - e_f) = x(1 - e_g)$ . Thus, having either majority or minority bifunctional units leads to different entanglement factors and, consequently, network properties.

## A more general polyurethane case

In order to illustrate the possibilities of the theory further, consider now a more complex system with a distribution of functionalities: tri-, bi-, and monofunctional isocyanates, as well as bi- and monofunctional diols. Let  $\varphi_{I3}$ ,  $\varphi_{I2}$ , and  $\varphi_{I1}$  denote the fractions of each isocyanate type,  $\varphi_{D2}$  and  $\varphi_{D1}$  the fractions of diols, with  $\varphi_{I3} + \varphi_{I2} + \varphi_{I1} = 1$  and  $\varphi_{D2} + \varphi_{D1} = 1$ . Let again  $n_I$  and  $n_D$  denote the molar fractions of isocyanates and diols, whatever their types, with  $n_I + n_D = 1$ , and assume equal reactivities. The ratio between the numbers of NCO and OH groups in the mixture, that is again supposed not to exceed 1, and that is also the ratio of the number of NCO and OH groups that have reacted, is given by

$$r = \frac{\bar{f}_I}{\bar{f}_D} \frac{n_I}{n_D} \quad (59)$$

using the average functionalities  $\bar{f}_I = 3\varphi_{I3} + 2\varphi_{I2} + \varphi_{I1}$  and  $\bar{f}_D = 2\varphi_{D2} + \varphi_{D1}$ . The probability that an isocyanate unit selected at random from the mixture has  $k$  reacted groups combines the probabilities to get each type of isocyanates and therefore is the coefficient of  $z^k$  in the following polynomial:

$$F_{0I}(z) = \varphi_{I3}(1 - x + xz)^3 + \varphi_{I2}(1 - x - xz)^2 + \varphi_{I1}(1 - x + xz) \quad (60)$$

and similarly for a diol selected at random:

$$F_{0D}(z) = \varphi_{D2}(1 - rx + rxz)^2 + \varphi_{D1}(1 - rx + rxz). \quad (61)$$

Computing the probabilities for an isocyanate or a diol to have reacted more than once must owe to the fact that, for instance, a randomly picked NCO group has a probability  $3\varphi_{I3}/\bar{f}_I$  to belong to a trifunctional isocyanate. Similarly, it has a probability  $2\varphi_{I2}/\bar{f}_I$  to belong to a bifunctional isocyanate, and a probability  $\varphi_{I1}/\bar{f}_I$  to belong to a monofunctional isocyanate. Therefore, the probabilities for a unit to have established more than one link are given by the following polynomials:

$$F_I(z) = \frac{1}{\bar{f}_I} [3\varphi_{I3}(1 - x + xz)^2 + 2\varphi_{I2}(1 - x + xz) + \varphi_{I1}] \quad (62)$$

and

$$F_D(z) = \frac{1}{\bar{f}_D} [2\varphi_{D2}(1 - rx + rxz) + \varphi_{D1}] \quad (63)$$

for isocyanates and diols, respectively. More generally,  $F(z)$  deduces from  $F_0(z)$  as

$$F(z) = \frac{F'_0(z)}{F'_0(1)} \quad (64)$$

where  $F'_0(z)$  is the derivative of  $F_0(z)$ . This concise relation is a further interest of using probability distribution functions to describe network formation, and it can be checked that (62) and (63) are recovered, as well as (3) and (28).

The probabilities of extinction  $e_I$  and  $e_D$  are given by the coupled equations  $e_I = F_I(e_D)$  and  $e_D = F_D(e_I)$ , since it suffices to express that the additional links of a unit that has already reacted once have finite continuations, with an alternation of isocyanate and diol. Therefore,

$$e_I = \frac{1}{\bar{f}_I} [3\varphi_{I3}(1 - x + xe_D)^2 + 2\varphi_{I2}(1 - x + xe_D) + \varphi_{I1}] \quad (65)$$

and

$$e_D = \frac{1}{\bar{f}_D} [2\varphi_{D2}(1 - rx + rxe_I) + \varphi_{D1}]. \quad (66)$$

The special role played by monofunctional molecules may be noted: they contribute to the extinction probability with their share in the average functionality, since they cannot establish new links after they have reacted once. These two equations give immediately

$$\frac{e_I - 1}{e_D - 1} = \frac{3\varphi_{I3}x^2(e_D - 1) + 6\varphi_{I3}x + 2\varphi_{I2}x}{\bar{f}_I} \quad \text{and} \quad \frac{e_D - 1}{e_I - 1} = \frac{2\varphi_{D2}rx}{\bar{f}_D} \quad (67)$$

hence

$$e_D = 1 - \frac{2}{3} \frac{3\varphi_{I3} + \varphi_{I2}}{\varphi_{I3}x} + \frac{\bar{f}_I \bar{f}_D}{6\varphi_{I3}\varphi_{D2}} \frac{1}{rx^3} \quad \text{and} \quad e_I = 1 - \frac{\bar{f}_D}{2\varphi_{D2}} \frac{1 - e_D}{rx}. \quad (68)$$

If there is no monofunctional unit,  $x = r = 1$  leads to  $e_D = e_I = 0$ : a perfect network is obtained, since no link has finite continuation. In contrast, if monofunctional units are present, they are dangling chains in the network, which is not perfect although the reaction is complete in stoichiometric conditions, and the extinction probability is not zero.

The fraction of reacted NCO groups at the gel point, obtained for  $e_D = e_I = 1$  to have infinite chains, is

$$x_g = \sqrt{\frac{1}{4r} \frac{\bar{f}_I \bar{f}_D}{(3\varphi_{I3} + \varphi_{I2}) \varphi_{D2}}} \quad (69)$$

and therefore a gel is obtained when reaction is complete if

$$r > \frac{\bar{f}_I \bar{f}_D}{4(3\varphi_{I3} + \varphi_{I2}) \varphi_{D2}}. \quad (70)$$

For instance, if  $\varphi_{I3} = \varphi_{I2} = 1/2$  and  $\varphi_{D2} = 1$  (then  $\varphi_{I1} = \varphi_{D1} = 0$ ), i.e., for an equal mixture of bi- and trifunctional isocyanates plus bifunctional diols only, a gel is obtained at the end of reaction if  $r > 5/8 = 0.625$ . Thus, distributed functionalities shift the gel point, which is 0.5 without bifunctional isocyanates as shown in the previous Section, to higher

values. This is due to rapidly saturated units, because of their small functionality, coming into play and slowing down the network formation.

Since probabilities  $e_D$  and  $1 - e_D$  merely have to be given to links with finite and infinite continuations, respectively, the fractions of the various types of isocyanate units when a gel has formed (active network nodes, elastically active chains, dangling chains, sol fraction) are given by the coefficients of the following polynomial:

$$\begin{aligned} \tilde{F}_{0I}(z) = & \varphi_{I3}[1 - x + xe_D + x(1 - e_D)z]^3 + \varphi_{I2}[1 - x + xe_D + x(1 - e_D)z]^2 + \\ & + \varphi_{I1}[1 - x + xe_D + x(1 - e_D)z] \end{aligned} \quad (71)$$

and for diols, similarly:

$$\tilde{F}_{0D}(z) = \varphi_{D2}[1 - rx + rxe_I + rx(1 - e_I)z]^2 + \varphi_{D1}[1 - rx + rxe_I + rx(1 - e_I)z]. \quad (72)$$

For instance, the total mass fraction of sol is

$$\begin{aligned} m_s = \frac{1}{M} [ & \varphi_{D1}(1 - rx + rxe_I)n_D M_{D1} + \varphi_{D2}(1 - rx + rxe_I)^2 n_D M_{D2} + \\ & + \varphi_{I1}(1 - x + xe_D)n_I M_{I1} + \varphi_{I2}(1 - x + xe_D)^2 n_I M_{I2} + \\ & + \varphi_{I3}(1 - x + xe_D)^3 n_I M_{I3}] \end{aligned} \quad (73)$$

using the molar mass of each component and the average molar mass of the mixture

$$\bar{M} = n_D(\varphi_{D1}M_{D1} + \varphi_{D2}M_{D2}) + n_I(\varphi_{I1}M_{I1} + \varphi_{I2}M_{I2} + \varphi_{I3}M_{I3}). \quad (74)$$

The number of moles of trifunctional isocyanate units that have formed triple nodes in the gel is

$$n = \varphi_{I3} x^3 (1 - e_D)^3 n_I = \frac{r \bar{f}_D \varphi_{I3}}{r \bar{f}_D + \bar{f}_I} x^3 (1 - e_D)^3 \quad (75)$$

since  $n_I = r \bar{f}_D / (r \bar{f}_D + \bar{f}_I)$  and  $n_D = \bar{f}_I / (r \bar{f}_D + \bar{f}_I)$ , and therefore the number of moles of elastically active chains per unit volume is

$$\nu_e = \frac{\rho}{\bar{M}} \frac{r \bar{f}_D}{r \bar{f}_D + \bar{f}_I} \left( 3\varphi_{I3} + \varphi_{I2} - \frac{\bar{f}_I \bar{f}_D}{4\varphi_{D2}} \frac{1}{rx^2} \right). \quad (76)$$

The total length of elastically active chains, which generalizes (49), is obtained by adding up the contributions of the three arms stemming from the network nodes, the two arms of tri- and bifunctional isocyanates along elastically active chains, and the diols in the latter chains:

$$\begin{aligned} \lambda(r, x) = & 3\tau x^3 (1 - e_D)^3 \varphi_{I3} n_I + 6\tau (1 - x + xe_D) x^2 (1 - e_D)^2 \varphi_{I3} n_I + \\ & + 2\tau x^2 (1 - e_D)^2 \varphi_{I2} n_I + r^2 x^2 (1 - e_I)^2 \varphi_{D2} n_D \end{aligned} \quad (77)$$

using the same unit length as in the previous Section. This expression can be simplified with (68):

$$\lambda(r, x) = \frac{\bar{f}_I \bar{f}_D^2}{4\varphi_{D2}} (1 - e_D)^2 \frac{2\tau + 1}{r \bar{f}_D + \bar{f}_I}. \quad (78)$$

The reference length is then, using (68) again:

$$\lambda(1, 1) = \frac{\bar{f}_I \bar{f}_D^2}{4\varphi_{D2}} \left( \frac{2}{3} \frac{3\varphi_{I3} + \varphi_{I2}}{\varphi_{I3}} - \frac{\bar{f}_I \bar{f}_D}{6\varphi_{I3}\varphi_{D2}} \right)^2 \frac{2\tau + 1}{\bar{f}_D + \bar{f}_I} \quad (79)$$

and  $T_e$  is obtained by squaring the ratio of these two quantities:

$$T_e = (1 - e_D)^4 \left( \frac{\bar{f}_D + \bar{f}_I}{r \bar{f}_D + \bar{f}_I} \right)^2 \left( \frac{6\varphi_{I3}\varphi_{D2}}{4\varphi_{D2}(3\varphi_{I3} + \varphi_{I2}) - \bar{f}_D \bar{f}_I} \right)^4 \quad (80)$$

which does not depend on  $\tau$ . The last term disappears and  $\bar{f}_D = 2$  when there is no mono-functional component: this generalizes (57) where the average functionality of isocyanates  $\bar{f}_I$  replaces the integer functionality  $g$ .

Thus, the expressions are more involved in the case of distributed functionalities, but of course the results of the previous Section are recovered when  $\varphi_{I3} = \varphi_{D2} = 1$  and therefore  $\varphi_{I2} = \varphi_{I1} = \varphi_{D1} = 0$ .

## Concise procedure

As could be observed, the statistical theory of network formation cannot be reduced to a small set of general formulae, for they differ in each case considered. Empirical adaptation of known results to new conditions, even close apparently, is risky and should be avoided. Nevertheless, the procedure to follow can be adapted in a very systematic manner, since it proceeds in 6 steps:

1. Write, for each chemical species, the polynomial that uses as coefficients the probabilities to have the various numbers of reacted groups.
2. Deduce, by taking and normalizing the derivative, the polynomial that uses as coefficients the probabilities, for each chemical species, to have additional reacted groups after a first group has reacted.
3. Use this polynomial to compute the probability that a reacted group leads to a finite branch, for each chemical species.
4. Deduce the gel condition by writing that these probabilities reach the critical value of 1, below which infinite chains are allowed.
5. Rewrite the initial polynomial for each chemical species, replacing the dummy variable  $z$  by the expression  $e + (1 - e)z$  that uses the probability of extinction of the other chemical species.
6. Deduce the fractions of interest in the mixture while reaction proceeds: sol fraction, active nodes, elastically active chains, dangling chains, trapped entanglements, etc.

In the present exposition, notations differ slightly from those employed in the literature, where several dummy variables  $z$  are introduced simultaneously, or where the coefficient of  $z^k$  is defined from the  $k$ -th derivative of the polynomial, for instance, which did not

seem necessary here. Moreover, the gel condition has been introduced more simply than by using additional polynomials or computing a determinant, as is frequently done since [8]. Despite these changes, the results are the same as in the literature, for instance (14) corresponds to (3.33) in [7] and (38) to (3.86), using the reciprocal definition of  $r$ . Similarly, (68) corresponds to (67) of [5] in the  $\varphi_{D1} = 0$  case, using the reciprocal definition of  $r$  too, (69) corresponds to (64), (73) to (68) and (76) to (74). These results are also recovered in page 314 of [4] but by reversing the roles of isocyanates and diols, just as in the appendix of [6].

## Examples of straightforward application of the procedure

The 6-step procedure of the previous Section is applied below to three cases with various complexities, in a straightforward manner which assumes that the above theory has been studied.

### Polyurethane considered in [6]

The mixture is composed of triols with either 3 or 2 functional groups, and bifunctional diisocyanates<sup>3</sup>. Therefore, with  $r = 2n_I/((\varphi + 2)n_T)$ , using  $\varphi$  for  $\varphi_3$  for brevity and consequently  $\varphi_2 = 1 - \varphi$ , step 1 gives

$$F_{0I}(z) = (1 - x + xz)^2 \quad F_{0T}(z) = \varphi(1 - rx + rxz)^3 + (1 - \varphi)(1 - rx + rxz)^2 \quad (81)$$

hence (step2 )

$$F_I(z) = \frac{F'_{0I}(z)}{F'_{0I}(1)} = 1 - x + xz$$

$$F_T(z) = \frac{F'_{0T}(z)}{F'_{0T}(1)} = \frac{3\varphi(1 - rx + rxz)^2 + 2(1 - \varphi)(1 - rx + rxz)}{\varphi + 2} \quad (82)$$

leading to  $e_I = F_I(e_T)$  and  $e_T = F_T(e_I)$ , which give (step 3)

$$e_I = 1 - \frac{2}{3} \frac{2\varphi + 1}{\varphi r x} + \frac{\varphi + 2}{3\varphi r^2 x^3} \quad \text{and} \quad e_T = 1 - \frac{1 - e_I}{x} \quad (83)$$

with gelation for (step 4)

$$x_g = \sqrt{\frac{1}{2r} \frac{\varphi + 2}{2\varphi + 1}}. \quad (84)$$

Moreover (step 5),

$$\tilde{F}_{0I}(z) = F_{0I}(e_T + (1 - e_T)z) = [1 - x + xe_T + x(1 - e_T)z]^2 \quad \text{and}$$

$$\tilde{F}_{0T}(z) = F_{0T}(e_I + (1 - e_I)z) = \varphi[1 - rx + rxe_I + rx(1 - e_I)z]^3 + (1 - \varphi)[1 - rx + rxe_I + rx(1 - e_I)z]^2 \quad (85)$$

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<sup>3</sup>Fractions of additional monofunctional components are also considered in [6], but are not supplied; they are ignored here.

give, for instance (step 6)

$$n = \varphi r^3 x^3 (1 - e_I)^3 n_T \quad (86)$$

and

$$m_s = \frac{1}{\overline{M}} [(1 - \varphi)(1 - rx + rxe_I)^2 n_T M_{T2} + \varphi(1 - rx + rxe_I)^3 n_T M_{T3} + (1 - x + xe_T)^2 n_I M_I] \quad (87)$$

with

$$\overline{M} = n_T [(1 - \varphi) M_{T2} + \varphi M_{T3}] + n_I M_I. \quad (88)$$

One also has  $T_e = [\lambda(r, x)/\lambda(1, 1)]^2$  with

$$\lambda(r, x) = 3r^3 x^3 (1 - e_I)^3 \varphi n_T + 6(1 - rx + rxe_I) r^2 x^2 (1 - e_I)^2 \varphi n_T + 2r^2 x^2 (1 - e_I)^2 (1 - \varphi) n_T + \tau x^2 (1 - e_T)^2 n_I \quad (89)$$

by counting the constitutive elements of elastically active chains. The arms of triols are assumed to all have the same length, taken as unit, and  $\tau$  denotes the length of a diisocyanate. Using  $n_T = 2/[(\varphi + 2)r + 2]$  and  $n_I = (\varphi + 2)r/[(\varphi + 2)r + 2]$ , deduced from the definition of  $r$  and from  $n_D + n_I = 1$ , this expression simplifies into

$$\lambda(r, x) = (1 - e_I)^2 \frac{\varphi + 2}{(\varphi + 2)r + 2} r (\tau + 2) \quad (90)$$

giving, finally

$$T_e = r^2 (1 - e_I)^4 \left[ \frac{\varphi + 4}{(\varphi + 2)r + 2} \right]^2 \quad (91)$$

which does not depend on  $\tau$ . It may be noted that this result can also be obtained by replacing the integer functionality  $g$  in (58) by the average functionality  $\varphi + 2$ .

These results do recover those given in the appendix of [6] when monofunctional units are ignored, with the reciprocal definition for  $r$ . Similarities may also be noted with the results given above in the last polyurethane case studied above, when monofunctional molecules are ignored: the gel condition, for instance, or the number of active nodes. For the latter,  $rx$  replaces  $x$ , in addition to the roles of alcohols and isocyanates being reversed, what could be missed in an empirical adaptation to the present chemical system.

In the special case where all triols are trifunctional ( $\varphi = 1$ ), there is also a similitude with the first, simple, polyurethane case considered above, by reversing the roles of the two components since the majority component is trifunctional now. For instance, the entanglement factor (91) becomes

$$T_e = \frac{1}{r^2 x^4} \left( 2 - \frac{1}{rx^2} \right)^4 \left( \frac{5}{3r + 2} \right)^2 \quad (92)$$

instead of (51). As shown in Figure 7,  $T_e$  is larger than with reversed functionalities, which allows more significant changes of the  $G(r)$  function by tuning parameters  $h$  and  $\varepsilon$  in (19).

### Tetrafunctional monomer

Up to this point, functionalities lower than 4 were considered, but it is interesting to observe the qualitative changes that are induced by a functionality of 4. In this Section, the simple case of the condensation of a 4-functional monomer is considered. For convenience, a star-shape with all arms of the same length is assumed. The procedure starts from (step 1)

$$F_0(z) = (1 - x + xz)^4 \quad \text{hence (step 2)} \quad F(z) = \frac{F'_0(z)}{F'_0(1)} = (1 - x + xz)^3 \quad (93)$$

and (step 3) condition  $e = F(e)$  leads, after simplification by  $1 - e$ , to a second degree equation with respect to  $1 - e$  (note that it is often simpler to compute  $1 - e$  than  $e$ ):

$$x^3(1 - e)^2 - 3x^2(1 - e) + 3x - 1 = 0 \quad (94)$$

where a single root ensures that  $e = 0$  when  $x = 1$  (perfect network, all chains are infinite and extinction probability is zero):

$$1 - e = \frac{3x - \sqrt{x(4 - 3x)}}{2x^2} \quad (95)$$

which does lead to the expected gel condition (11) when  $1 - e = 0$ , i.e.,  $x_g = 1/3$  (step 4). Finally (step 5),

$$\tilde{F}_0(z) = F_0(e + (1 - e)z) = [1 - (1 - e)x + (1 - e)xz]^4 \quad (96)$$

leads immediately (step 6) to the sol fraction  $s$ , the fractions of monomers involved in dangling chains  $d$  and of elastically active chains  $a$  (uncounting nodes):

$$s = [1 - (1 - e)x]^4 \quad d = 4[1 - (1 - e)x]^3(1 - e)x \quad a = 6[1 - (1 - e)x]^2(1 - e)^2x^2 \quad (97)$$

and, eventually, the fractions of monomers that are active nodes of the network, with either 3 or 4 reacted groups, are given by:

$$n_3 = 4[1 - (1 - e)x](1 - e)^3x^3 \quad \text{and} \quad n_4 = (1 - e)^4x^4. \quad (98)$$

Therefore, the total fraction of monomers that are active nodes, and their average functionality are given by

$$n = n_3 + n_4 = [4 - 3(1 - e)x](1 - e)^3x^3$$

$$\text{and} \quad f_n = \frac{3n_3 + 4n_4}{n} = 4 \frac{3 - 2(1 - e)x}{4 - 3(1 - e)x}. \quad (99)$$

Figure 8 shows that this average functionality, which of course is 4 for a perfect network ( $x = 1$ ), takes its lowest possible value of 3 at the gel point ( $x = 1/3$ ) and varies nonlinearly when reaction proceeds.

The respective weights of the two terms in the expression (19) of the shear modulus are interesting to discuss. When  $h$  varies from 0 to 1, the first term evolves from  $f_n n / 2$ , the number of elastically active chains (since each one connects two nodes, and  $f_n n$  chains

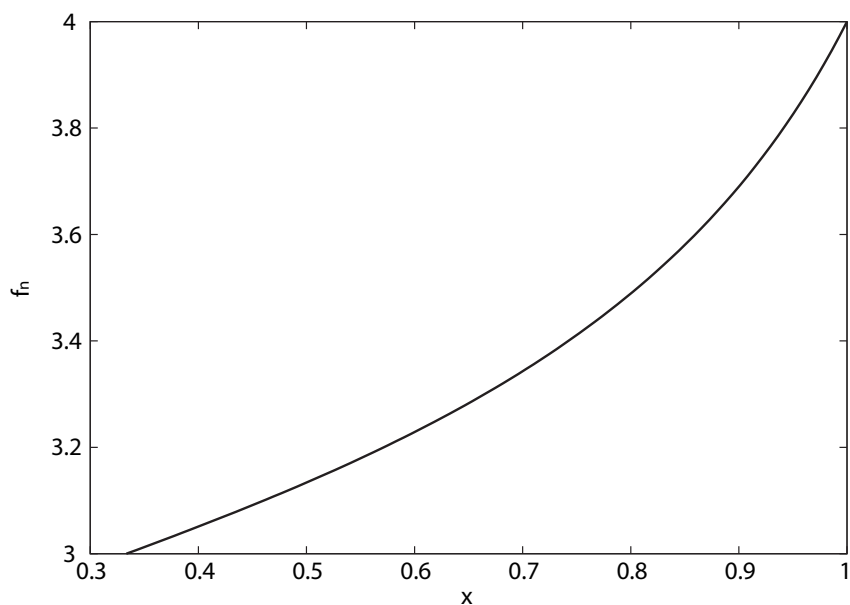


Figure 8. Variation of the average functionality of active nodes during condensation of tetrafunctional monomers.

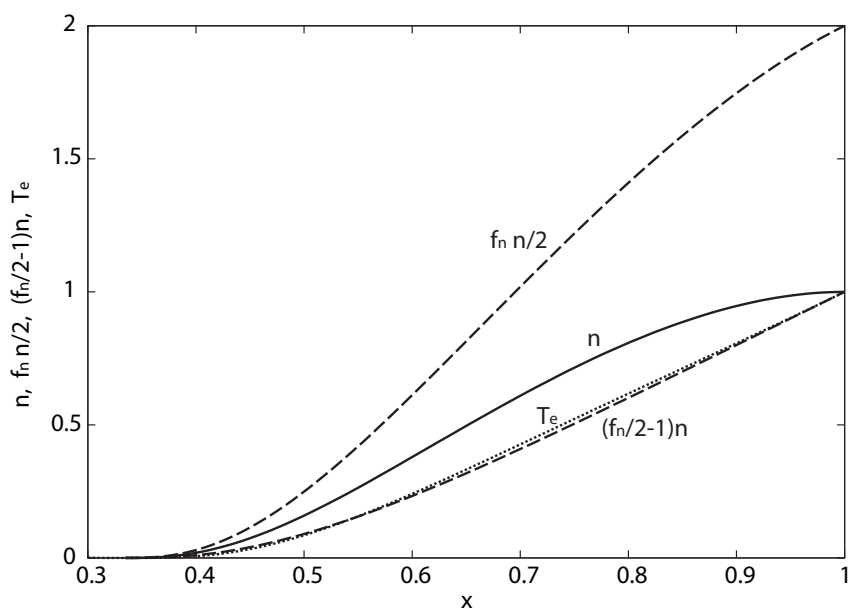


Figure 9. Variations of the fraction of monomers that are active nodes (unbroken line), of the two limit values of the first term in the expression of the shear modulus (broken lines), and of the entanglement factor (dotted line), while condensation of tetrafunctional monomers proceeds.



stem from the latter) to  $(f_n/2 - 1)n$ , the value given by the phantom network theory [13]. The entanglement factor is obtained easily from the total length of elastically active chains, which can be written as follows by using the length of a monomer arm as unit:

$$\lambda(x) = 4n_4 + 3n_3 + 2a = 4(1 - e)^2x \quad (100)$$

thus  $\lambda(1) = 4$  and

$$T_e = x^2(1 - e)^4 \quad (101)$$

in concordance with (26). Figure 9 shows the variations of the two parts of the shear modulus, including the two limit cases for the first one. For comparison, the variations of the fraction of monomers that are active nodes is also shown. It can be observed that the term from the affine theory retains part of the downward concavity of the variations of the number of active nodes, which was absent in the cases studied up to this point with functionalities below 4. In contrast, the term from the phantom network theory exhibits an upward concavity. Its values are close to half the values for the affine theory, being exactly one half for perfect networks only (which is expected for tetrafunctional nodes). Its values are found close to the entanglement factor.

### Polyurethane considered in [15]

The system is composed of bifunctional diols and a mixture of tri- and quadriisocyanates. With  $r = (4 - \varphi)n_I/(2n_D)$ , where  $\varphi = \varphi_{I3}$  for conciseness and therefore  $\varphi_{I4} = 1 - \varphi$ , step 1 leads to:

$$F_{0I}(z) = (1 - \varphi)(1 - x + xz)^4 + \varphi(1 - x + xz)^3 \quad F_{0D}(z) = (1 - rx + rxz)^2 \quad (102)$$

thus (step 2)

$$F_I(z) = \frac{F'_{0I}(z)}{F'_{0I}(1)} = \frac{4(1 - \varphi)(1 - x + xz)^3 + 3\varphi(1 - x + xz)^2}{4 - \varphi}$$

$$F_D(z) = \frac{F'_{0D}(z)}{F'_{0D}(1)} = 1 - rx + rxz. \quad (103)$$

Hence  $e_I = F_I(e_D)$  and  $e_D = F_D(e_I)$ , which give readily (step 3)

$$e_D = 1 - \frac{3(4 - 3\varphi)rx - \sqrt{\Delta}}{8(1 - \varphi)rx^2} \quad \text{and} \quad e_I = 1 - \frac{1 - e_D}{rx} \quad (104)$$

since a single root of the second degree equation to solve ensures  $e_D = e_I = 0$  if  $x = r = 1$  (no finite chain in the perfect network), with

$$\Delta = (4 - \varphi)r[16(1 - \varphi) - 3(4 - 5\varphi)rx^2]. \quad (105)$$

The gel point yields, when  $e_D = e_I = 1$  (step 4):

$$x_g = \sqrt{\frac{1}{6r} \frac{4 - \varphi}{2 - \varphi}}. \quad (106)$$

Next (step 5),

$$\begin{aligned}\tilde{F}_{0I}(z) &= F_{0I}(e_D + (1 - e_D)z) = \\ &= (1 - \varphi)[1 - x + xe_D + x(1 - e_D)z]^4 + \varphi[1 - x + xe_D + x(1 - e_D)z]^3 \\ \text{and } \tilde{F}_{0D}(z) &= F_{0D}(e_I + (1 - e_I)z) = [1 - rx + rxe_I + rx(1 - e_I)z]^2\end{aligned}\quad (107)$$

give, for instance (step 6),

$$n = [4(1 - \varphi)(1 - x + xe_D)x^3(1 - e_D)^3 + \varphi x^3(1 - e_D)^3 + (1 - \varphi)x^4(1 - e_D)^4]n_I \quad (108)$$

since active nodes are formed by triisocyanates and quadriisocyanates, and the latter may have either 3 (first  $z^3$  term in  $\tilde{F}_{0I}(z)$ ) or 4 (single  $z^4$  term in  $\tilde{F}_{0I}(z)$ ) reacted NCO groups. This expression can also be recast as

$$n = (1 - e_D)^3 x^3 [4 - 3\varphi - 3(1 - \varphi)(1 - e_D)x]n_I. \quad (109)$$

The sol fraction is given by

$$\begin{aligned}m_s &= \frac{1}{\overline{M}} [(1 - rx + rxe_I)^2 n_D M_D + \\ &+ (1 - \varphi)(1 - x + xe_D)^4 n_I M_{I4} + \varphi(1 - x + xe_D)^3 n_I M_{I3}]\end{aligned}\quad (110)$$

with

$$\overline{M} = n_D M_D + (1 - \varphi)n_I M_{I4} + \varphi n_I M_{I3}. \quad (111)$$

All these results agree with appendix 2 of [5] in the  $\varphi = 1$  case.

The entanglement factor  $T_e = [\lambda(r, x)/\lambda(1, 1)]^2$  can be deduced from the terms of  $\tilde{F}_{0I}(z)$  and  $\tilde{F}_{0D}(z)$  where  $z$  is raised to at least 2, which gives

$$\begin{aligned}\lambda(r, x) &= 4\tau(1 - \varphi) \times \\ &\times [x^2(1 - e_D)^2 + 3(1 - x + xe_D)x(1 - e_D) + 3(1 - x + xe_D)^2]x^2(1 - e_D)^2 n_I + \\ &+ 3\tau\varphi[x(1 - e_D) + 2(1 - x + xe_D)]x^2(1 - e_D)^2 n_I + r^2 x^2(1 - e_I)^2 n_D\end{aligned}\quad (112)$$

assuming that all arms of isocyanate units have the same length, which is a fraction  $\tau$  of the length of a diol. Using  $n_I = 2r/(2r + 4 - \varphi)$  and  $n_D = (4 - \varphi)/(2r + 4 - \varphi)$ , which yield from the definition of  $r$ , the previous equation reduces to

$$\lambda(r, x) = \frac{2\tau + 1}{2r + 4 - \varphi} (1 - e_D)^2 (4 - \varphi) \quad (113)$$

with, consequently,  $\lambda(1, 1) = (2\tau + 1)(4 - \varphi)/(6 - \varphi)$  and

$$T_e = \left( \frac{6 - \varphi}{2r + 4 - \varphi} \right)^2 (1 - e_D)^4 \quad (114)$$

which does not depend on  $\tau$ . Here again,  $T_e$  is obtained from (57) if the average functionality ( $\bar{f} = 4 - \varphi$ ) replaces the integer functionality of the component that is not bifunctional.

When  $x = 1$  (reaction is complete) and  $\varphi = 0$ , i.e., there is no triisocyanate, therefore all nodes are tetrafunctional and  $r = 2n_I/n_D$ , the gel point is obtained for  $r = 1/3$  and one has merely

$$e_D = -\frac{1}{2} + \sqrt{\frac{1}{r} - \frac{3}{4}} \quad \text{and} \quad n = (1 - e_D)^3(1 + 3e_D)n_I \quad (115)$$

with an entanglement factor given by

$$T_e = 9 \frac{(1 - e_D)^4}{(r + 2)^2} \quad (116)$$

which is a special case of (57) when  $f = 4$ . Figure 10 illustrates the variations of the number fraction of active nodes, with downward concavity for large  $r$  values, and of their average functionality

$$f_n = \frac{n_I}{n} [4(1 - e_D)^4 + 12e_D(1 - e_D)^3] = 4 \frac{1 + 2e_D}{1 + 3e_D}. \quad (117)$$

The above relations lead to the curves in Figure 11, where the two parts of the expression of the shear modulus are shown, with two limit cases for the first one, as well as the entanglement factor. Trends can be compared with those already found in the previous Section, where 4-functional units were also present, but now when  $r$  varies. The approximate 1/2 ratio between the two variants for the first part of the shear modulus is observed, but the downward concavity found for  $n/n_I$  is significantly weakened by the product with  $n_I = 2r/(2r + 1)$  and  $f_n$ . Moreover, the entanglement factor now differs significantly from the other curves.

These results may also be compared with those given by the recursive approach of [2] as summarized in appendix 2 of [3], for instance. The same definition is used for  $r$ , and  $P(F_B^{\text{out}})$  corresponds to  $e_D$ . Actually, relations (70) and (78) of [3] do coincide with (104) when  $\varphi = 0$  and  $\varphi = 1$ , respectively. Similarly, the numbers of active nodes obtained in [2] agree with (109). In contrast, the entanglement factor in [3] misses the  $(2 + f)/(2r + f)$  squared term that was obtained in (57) from different molar fractions of constituents being involved in the perfect and imperfect networks off stoichiometry. This may be due to different definitions of the reference network, and the two approaches nevertheless lead to the same results in stoichiometric conditions ( $r = 1$ ).

## Conclusion

An introduction has been given to the statistical theory of polymer network formation that uses probability generating functions, starting from the few mathematical notions that are required and ending with a simple procedure that can be followed in many cases of practical interest. It has been shown on several detailed examples of various complexities that, even if the theory may seem complicated at first sight, its use is quite simple in many circumstances. Emphasis has been put here on connections with the theory of rubber elasticity, with special attention devoted to the trapped entanglement factor, but other applications can be considered, of course, by taking advantage of the various statistical features of the gel

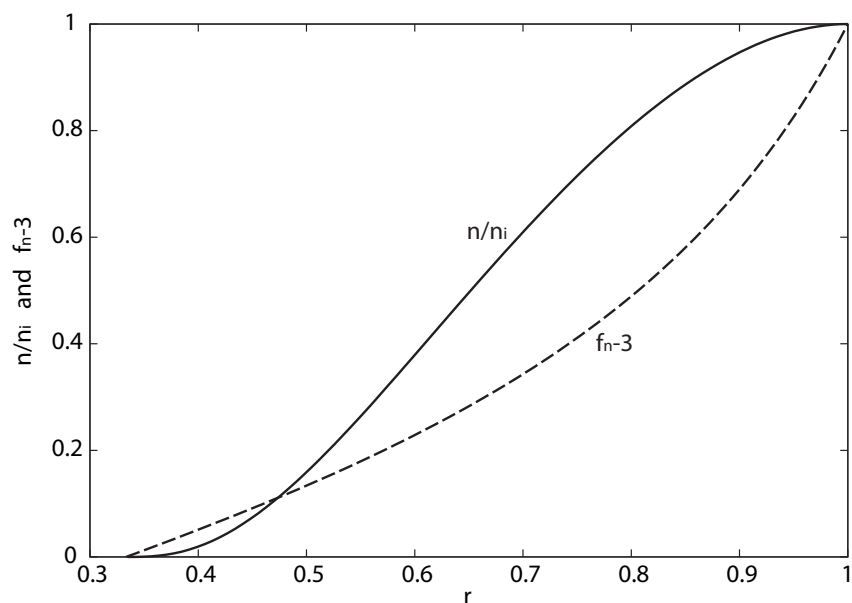


Figure 10. Fraction  $n/n_I$  of isocyanates that are active nodes of the network (unbroken line) and average functionality of these nodes (broken line), when reaction is complete, as functions of the composition of a quadriisocyanate-diol mixture.

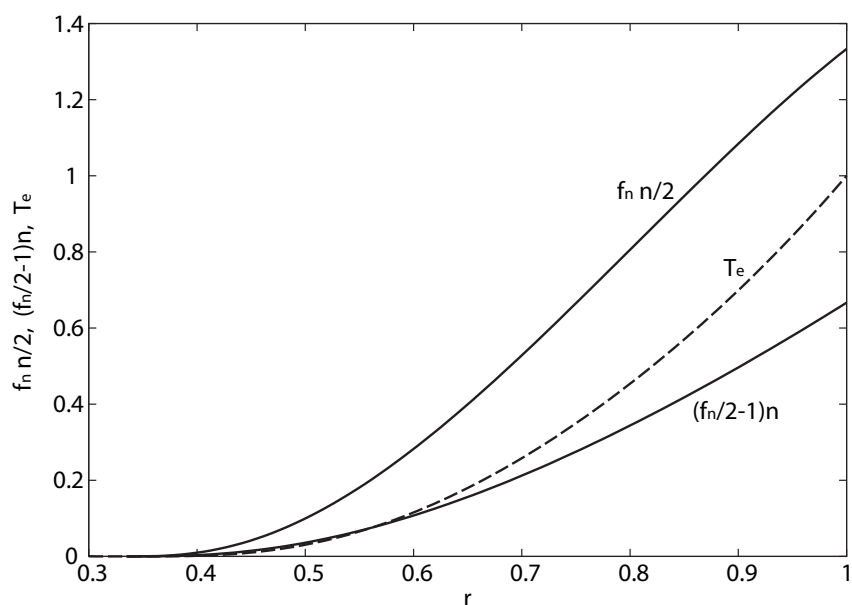


Figure 11. Limits of the first term in the expression of the shear modulus (unbroken lines), for  $h = 0$  (upper curve) and  $h = 1$  (lower curve), for complete reaction, as functions of the composition of a quadriisocyanate-diol mixture. The entanglement factor  $T_e$  is also shown (broken line).

and sol phases that are obtained. The variation of the molecular weight distribution in the latter with reaction extent, for instance, is of fundamental importance.

The present exposition is far from being exhaustive and has been limited to a mere introduction. Examples have been given on stepwise polymerization of homopolymers of various uniform functionalities, and on different polyurethane systems, including distributed functionalities, but random crosslinking of linear polymer molecules has not been considered, for instance. This important process, of which vulcanization of rubber is an example, has a close connection with complete condensation of (minority) tetrafunctional and (majority) bifunctional units, as demonstrated by P.J. Flory [16]. Equal reactivities have also been assumed in this Chapter, whereas this may not apply to important systems; the examples considered in [17] and [7], where two reactivities are considered, are interesting in this respect. More importantly, cyclization has been neglected, although intramolecular reactions may play an important role in many cases. This phenomenon leads to somewhat more elaborate developments than what could be covered in this Chapter, and the reader may refer to the work of R. Stepto ([18], for instance) and to the review by K. Dušek [4] for more details.

## References

- [1] Macosko, C.W.; Miller D.R. *Macromolecules* 1976, 9, 199-206.
- [2] Miller D.R.; Macosko C.W. *Macromolecules* 1976, 9, 206-211.
- [3] Queslel J.P.; Mark. J.E. *Adv. Polym. Sci.* 1984, 65, 135-176.
- [4] Dušek K. In *Telechelic Polymers: Synthesis and Applications*; Goethals, E.; Ed.; CRC Press: Boca raton, FL, 1989; pp 289-360.
- [5] Dušek K.; Dušková M.; Fedderly J.J.; Lee G.F.; Hartmann B. *Macromol. Chem. Phys.* 2002, 203, 1936-1948.
- [6] Ilavský M.; Dušek K. *Polymer* 1983, 24, 981-990.
- [7] Pascault J.-P.; Sautereau H.; Verdu J.; Williams R.J.J. *Thermosetting Polymers*; Marcel Dekker Inc.: New York, NY, 2002.
- [8] Gordon M. *Proc. Roy. Soc. London* 1962, A268, 240-259.
- [9] Harris T.E. *The Theory of Branching Processes*, Springer: Berlin, 1963.
- [10] Flory P.J. *J. Amer. Chem. Soc.* 1941, 63, 3083-3090.
- [11] Flory P.J. *J. Amer. Chem. Soc.* 1941, 63, 3091-3096.
- [12] Dossin L.M.; Graessley W.W. *Macromolecules* 1979, 12, 123-130.
- [13] Flory P.J. *Proc. Roy. Soc. London* 1976, A351, 351-380.
- [14] Langley N.R. *Macromolecules* 1968, 1, 348-352.

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- [15] Fayolle B.; Gilormini P.; Diani J. *Colloid Polym. Sci.* 2010, 288, 97-103.
- [16] Flory P.J. *Principles of Polymer Chemistry*, Cornell University Press: Ithaca, NY (1953).
- [17] Ilavský M.; Šomvársky J.; Bouchal K.; Dušek K. *Polym. Gels Networks* 1993, 1, 159-184.
- [18] Cail J.L.; Stepto R.F.T. *Polym. Bull.* 2007, 58, 15-25.